# Coupling between superconductivity and structural deformation in $La_{2-x}Sr_xCuO_4$ ($x \sim 0.13$)

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Capacitance-dilatometer measurements of the anisotropic thermal expansion on a superconducting single crystal of $La_{2-x}Sr_xCuO_4$ ($x \sim 0.13$) show large anomalies at the structural transition from the high-temperature tetragonal to the low-temperature orthorhombic phase followed by smaller anomalies of the opposite sign at the superconducting phase transition. Neutron-diffraction experiments on the same crystal indicate that at $T_c$ the tilt of the $CuO_6$ octahedra related to the structural phase transition is frozen in.

A lot of effort has been made in the past years to examine the relation between superconductivity and the crystal lattice in the copper-oxide-based high-$T_c$ compounds. First indications for a response of the Cu-O coordination to the superconducting order have been found by several EXAFS measurements.[1-3] Ion channeling revealed anomalies at $T_c$ which were attributed to a different dynamical behavior of the Cu and O atoms in the normal and the superconducting states.[4,5] More recently changes in the atomic pair distribution function of several high-$T_c$ materials have been observed by powder neutron diffraction.[6-8] It was claimed that the local structure deviates from the standard structural models, and that these local distortions change at $T_c$. Direct indications for a structural response to the superconductivity have been observed by thermal expansion measurements on single crystals of $YBa_2Cu_3O_{7-x}$.[9,10] These experiments revealed a second-order-like anomaly in the temperature dependence of the orthorhombic distortion.

In this paper we present dilatometric thermal expansion measurements on a single crystal of $La_{1.87}Sr_{0.13}CuO_4$ which clearly show a coupling between the superconductivity and the crystal structure. Due to further neutron experiments done on the same crystal, it is possible to identify the microscopic effect in the crystal structure. The continuously increasing orthorhombic distortion and the $CuO_6$ tilt, which are related to the phase transition from the high-temperature tetragonal (HTT) to the low-temperature orthorhombic (LTO) phase, are stopped by the onset of superconductivity.

The large single crystal of composition $La_{1.87}Sr_{0.13}CuO_4$ has been grown by the traveling floating-zone method.[11,12] The superconducting transition temperature of this crystal, $T_c = 32.5(5)$ K, was determined by specific-heat measurements.[13] The crystal has been cut to a size of $2 \times 3 \times 10$ mm$^3$, with the surfaces parallel to (0 0 1) or (1 1 0) planes in the orthorhombic notation. Thermal expansion measurements were performed with a capacitance dilatometer[13] (resolution of $\Delta l / l < 10^{-9}$) along [0 0 1] and [1 1 0] directions.

Neutron diffraction experiments were performed at the ORPHEE reactor, Saclay. The room-temperature tetragonal lattice constants are $a = 3.781(2)$ Å and $c = 13.228(8)$ Å, in agreement with results obtained on powders.[14] It should be mentioned that some misoriented fractions were observed in the crystals. They deviate from the main orientation by about 3°, which is too small to influence the macroscopic measurement of the thermal expansion. Integrated Bragg intensities of the superstructure reflections (5 2 2) and (2 5 2) were measured on the four-circle diffractometer P110 installed at the hot source ($\lambda = 0.83$ Å). Intensities of the (302) and (400) reflections were measured on a triple axis spectrometer (4F.2, $\lambda = 2.36$ Å).

The thermal expansion coefficient parallel to the $c$ axis, $\alpha_{[001]}$, is displayed in Fig. 1. The transition temperature $T_{t-o}$ of the HTT-LTO phase transition has been determined by intensity measurements of the (3 0 2) superstructure reflection, $T_{t-o} = 196.5(5)$ K (in good accordance with the $c_p$ measurements). At this temperature $\alpha_{[001]}$ shows a clear anomaly with a dip and a discontinuity. Below $T_{t-o}$ it decreases almost linearly with decreasing temperature. At the superconducting transition temperature $T_c$, $\alpha_{[001]}$ drops down to a slightly negative

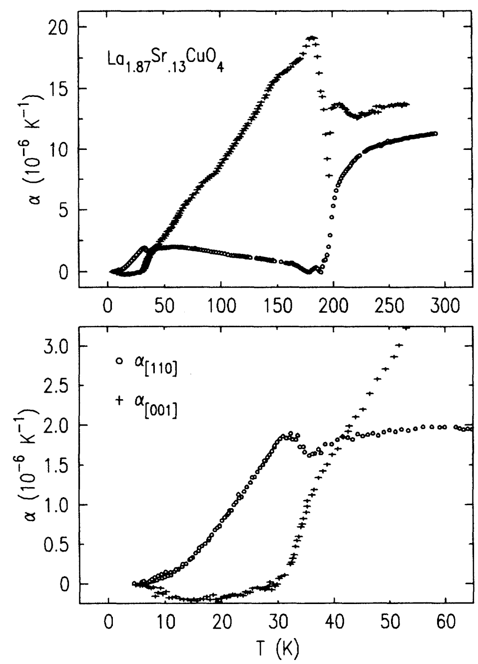


FIG. 1. Thermal expansion coefficient $\alpha$ of $La_{1.87}Sr_{0.13}CuO_4$ parallel to the [001] direction and parallel to the [110] direction.

value. Along the [1 1 0] direction a similar behavior is observed (Fig. 1). On cooling a first anomaly occurs at the structural phase transition $T_{t-o}$, where $\alpha_{[110]}$ drops to almost zero. In the LTO phase $\alpha_{[110]}$ increases but remains small. Again a second anomaly is observed at $T_c$, where $\alpha_{[110]}$ displays a discontinuity leading to an excess thermal expansion in the superconducting phase. Hence, $\alpha$ shows anomalies at $T_{t-o}$ followed by anomalies of the opposite sign at $T_c$ in both directions.

As the crystal shows a typical twin structure[12], we recorded for one of the superstructure reflections both twin law connected reflections (522) and (252). The intensities are displayed in Fig. 2 as function of temperature. In the temperature range from 60 K down to $T_c$, the intensities of both superstructure reflections increase on cooling. This increase is significantly lower in the region below $T_c$. At the (400) reflection we find an almost constant intensity in the examined temperature range.

The discussion of the structural phase transitions in the framework of the Landau-Ginzburg free energies has been developed in the past few years for the sequence of phase transitions in $La_{2-x}Ba_xCuO_4$ (Refs. 15 and 16) and before for MAMC,[17] where the symmetry sequences are the same. The Landau-Ginzburg free energy consists of three parts: $F_Q$, for series expansion in powers of the order parameter; $F_E$, the elastic energy due to strain, and $F_c$, the coupling between the order parameter and the spontaneous strains. Quoting the results given in Ref. 17 we use

$$F_C=\gamma_1(u_{xx}+u_{yy})(Q_1^2+Q_2^2)+\gamma_2 u_{zz}(Q_1^2+Q_2^2)+\gamma_3 u_{xy}(Q_1^2-Q_2^2) , \quad (1)$$

where $u_{ij}$ are the strains in the high-temperature notation

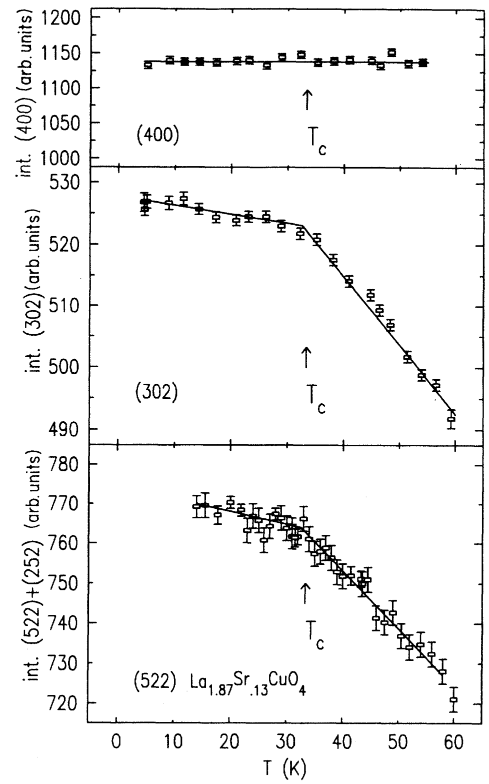


FIG. 2. The temperature dependence of the intensities of several Bragg reflections. For (522) the sums of the integrated intensities of the (5 2 2) and (2 5 2) reflections are displayed. The solid lines are guides for the eye.

(I4/mmm, $D_{4h}^{17}$) and $Q_1$ and $Q_2$ the components of the order parameter. These components describe the tilt of the $CuO_6$ octahedra around the tetragonal [110] and [$1\bar{1}0$] axes.[15] Here we need only to consider the transition to the LTO phase, which is characterized by either $Q_1=0$ and $Q_2\neq 0$ or $Q_1\neq 0$ and $Q_2=0$ and therefore by only one component, $Q_i$. The condition that the sample has to be stress free leads to the proportionality of the three strains $u_{xx}+u_{yy}$, $u_{zz}$, and $u_{xy}$ to the square of the order parameter $Q_i^2$. The strains $u_{ij}$ can be transformed into relations for the orthorhombic lattice constants:

$$\left[\frac{a+b}{2a_t}-1\right]\propto Q_i^2 , \quad (2)$$

$$\left[\frac{c}{c_t}-1\right]\propto Q_i^2 , \quad (3)$$

$$\left[\frac{a-b}{2a_t}\right]\propto Q_i^2 , \quad (4)$$

where $a_t$ and $c_t$ are the untransformed tetragonal lattice constants. In (4) one can approximate $2a_t$ by $a+b$, which yields the proportionality between the orthorhombic strain, $\epsilon$, and $Q_i^2$, as confirmed by Böni *et al.*[18] The observed thermal expansion of the twinned crystal corresponds to the strains $u_{xx}+u_{yy}$ and $u_{zz}$ [relations (2) and (3)]. The large anomalies at $T_{t-o}$ show for the first time that the coupling between the order parameter and these both strains, $u_{xx}+u_{yy}$ and $u_{zz}$, is significant and has to be considered in a quantitative Landau theory.

The tilt of the $CuO_6$ octahedra in the LTO phase causes an additional shortening of the $c$ axis due to the small thermal expansion of the La-O(2) and Cu-O(2) bonds.[19] This shortening is coupled to $Q_i$ by (3). Assuming a mean-field behavior of the order parameter $Q_i^2 \propto (1-T/T_{t-o})^{2\beta}$ with $2\beta=1.0$, there should be a positive shift in $\alpha_{[001]}$ on cooling. For the 3D-XY model with cubic anisotropy[20] the effect of fluctuations reduces the critical exponent and hence causes a divergence of $\alpha_{[001]}$, which will be smeared out by precursor effects. With the exception of the dip at $T_{t-o}$, this corresponds to the observed behavior, Fig. 1. The influence of the precursor effects seems to be very important at this transition. In the LTO phase there remains always an additional thermal expansion due to the continuous increase of $Q_i$ on cooling.

The dip at $T_{t-o}$ is not understood yet and several explanations are possible. The formation of the twin domain structure due to the phase transition has been studied on this crystal and was found to be discontinuous at $T_{t-o}$.[12] This may explain a discontinuous length change of the entire crystal. Another possibility is a first-order contribution of the phase transition which might be strain induced.

A structure analysis of $La_2CuO_4$ shows that only the $LaO_9$ polyhedron contracts in the LTO phase, whereas the $CuO_6$ octahedron remains almost unchanged or even becomes larger on cooling,[19] which is in agreement with the microscopic model of bond length mismatch.[21] This explains the decrease of the volume thermal expansion, $\alpha_v=2/3\alpha_{[110]}+1/3\alpha_{[001]}$, at $T_{t-o}$ on cooling, which is evident in our measurements and has already been shown in a similar dilatometer experiment on a polycrystalline sample by White *et al.*[22] The sign of the pressure dependence of $T_{t-o}$ calculated by the Ehrenfest relation[23] and the observed decrease of $\alpha_v$ is in qualitative agreement with the direct measurements.[24] The observed elongation in the [1 1 0] direction with respect to the untransformed tetragonal lattice does not fit into the picture of a rigid tilt of the $CuO_6$ octahedra. It implies a lengthening of the in-plane Cu-O bonds on cooling in the LTO phase. This influence of the phase transition on Cu-O bond lengths indicates further that the coupling between the deformation and the electronic system may not be negligible.

Hence, in both directions [0 0 1] and [1 1 0], the continuous increase of $Q_i$ in the LTO phase yields additional terms in the thermal expansion (positive and negative, respectively), which are proportional to $dQ_i^2/dT$, see (2) and (3).

Concerning the anomalies at $T_c$, it is interesting to note that the anomalies are anisotropic with opposite sign for the [1 1 0] and [0 0 1] directions. Therefore, the anomaly in the volume expansion is almost canceled to $\Delta\alpha_v=1.7(5)\times10^{-7}$ K$^{-1}$ in qualitative agreement with results of Lang *et al.*[23] obtained on a powder sample of $La_{1.85}Sr_{0.15}CuO_4$ Our results of $\Delta\alpha_v$ and $\Delta C_p=0.16$ J/mol K combined according to the Ehrenfest relation yield a pressure dependence of $dT_c/dp=6(2)$ K/GPa in agreement with direct measurements of $dT_c/dp$.[25] Recently, measurements on aligned grains revealed that the dependence of $T_c$ on uniaxial stress parallel to the $c$ axis is negative,[26] which agrees nicely with the anisotropic anomalies and the sign of the discontinuity in $\alpha_{[001]}$ at $T_c$ (Fig. 1).

Below $T_c$ $\alpha_{[001]}$ is negative, it jumps at $T_c$ from negative to positive values. Also in undoped $La_2CuO_4$ a negative thermal expansion has been observed for the $c$ direction at low temperatures.[23] However in $La_2CuO_4$ $\alpha_{[001]}$ increases continuously with increasing temperature and becomes positive at about 15 K. At 32.5 K there is no anomaly which could be compared to the observation in the superconducting sample. The negative value of $\alpha_{[001]}$ at low temperatures may be explained in both compounds by the low frequency $CuO_6$ tilt modes. [A similar behavior has been reported for $YBa_2Cu_3O_{7-\delta}$ (Ref. 10) and $YBa_2Cu_4O_8$ (Ref. 27) in the $b$ direction.]

The intensities of the superstructure reflections (302) and (522) are caused by the small static displacements of the La/Sr and O sites in the LTO phase. Therefore these intensities are proportional to the square of the order parameter and hence to the orthorhombic deformation ($I \propto Q_i^2$). Their temperature dependence allows the determination of the critical exponent $\beta$.[18,28] Here we want only to discuss the behavior near $T_c$. The pronounced increase of the intensity renormalized to the extrapolated value at 0 K,

$$\frac{1}{I(0)}\left[\frac{dI}{dT}\right]=0.0018(2)\ \mathrm{K}^{-1}\quad \text{for } (302)$$

and

$$\frac{1}{I(0)}\left[\frac{dI}{dT}\right]=0.0016(2)\ \mathrm{K}^{-1}\quad \text{for } (522)\ ,$$

in the region from 50 K down to $T_c$ indicates a still growing lattice deformation and octahedron tilt on cooling. Below $T_c$ there remains only a small increase of the intensities,

$$\frac{1}{I(0)}\left[\frac{dI}{dT}\right]=0.0003(1)\ \mathrm{K}^{-1}\ .$$

Hence we conclude that in the superconducting phase the deformation related to the structural phase transition is almost completely frozen in.

Due to a freezing in of $Q_i$ in the superconducting phase, the additional terms in the thermal expansion coefficient proportional to $dQ_i^2/dT$ are canceled below $T_c$, thereby yielding anomalies at $T_c$. The opposite signs of the anomalies at $T_c$ and $T_{t-o}$ confirm this picture. Furthermore the ratios between the anomalies at $T_c$ and near to the structural phase transition are almost the same for $\alpha_{[001]}$, $\alpha_{[110]}$, and $dQ_i^2/dT$.[28] All observed anomalies at $T_c$ can be explained by the freezing in of the order parameter.

The freezing in of the structural order parameter at $T_c$ shows that in $La_{1.87}Sr_{0.13}CuO_4$ the superconductivity is coupled to the lattice deformation which starts at the structural phase transition. More generally one may conclude that the superconductivity is coupled with the tilt of the $CuO_6$ octahedra.

A freezing in of the orthorhombic deformation should cause an anomaly in the orthorhombic strain, which could not be detected in our experiment due to the twinning of the crystal. However Meingast *et al.*[10] observed such an anomaly on an untwinned crystal. This analogy suggests an influence of tilt modes in $YBa_2Cu_3O_{7-\delta}$ too. Changes in the local $CuO_6$ tilt structure at $T_c$ have also been proposed for $Tl_2Ba_2CaCu_2O_8$.[6]

A coupling between superconductivity and the octahedron tilt may be important for the discussion of the structural transition from the LTO into a low-temperature tetragonal (LTT) phase observed for $La_{2-x}Ba_xCuO_4$ (Ref. 15) and $La_{2-x-y}Nd_ySr_xCuO_4$.[29] It has been argued that the instability against this second-phase transition is intrinsically ionic,[30,31] whereas its occurrence may critically depend on the electronic system. There is a common instability which drives both phase transitions.[21] Therefore the LTO-LTT transition may be considered as the continuation of the HTT-LTO transition into another structural polymorph. Hence the same mechanism which causes a freezing in of the order parameter could also supress the LTO-LTT transition in the superconducting state.

In conclusion single-crystal thermal expansion and neutron diffraction experiments show that in $La_{1.87}Sr_{0.13}CuO_4$ there is a clear anisotropic response of the crystal structure to the onset of superconductivity. The continuous increase of the order parameter in the LTO phase is frozen in. These observations are experimental evidence for the significant coupling between the octahedron tilt and superconductivity in $La_{2-x}Sr_xCuO_4$.

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